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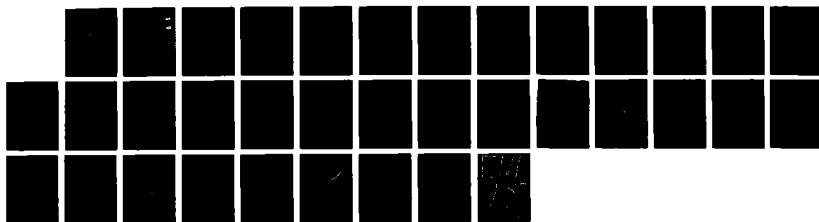
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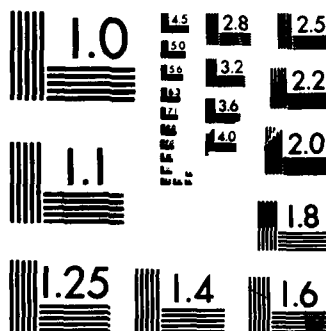
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THE ADSORPTION OF H_2 AND D_2 ON Fe(110) I:
HELIUM SCATTERING AS A PROBE OF ADSORPTION

by

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ABSTRACT

Results of thermal energy atom scattering (TEAS) measurements of H_2 and D_2 adsorption-desorption kinetics on Fe(110) are presented in detail, with emphasis on the strength and pitfalls inherent in this recently developed technique. It is shown that, for this system, adlayer coverage is directly related to the height of the specularly scattered peak from an incident helium atomic or deuterium molecular beam. The scattered peak height was used to monitor surface concentration as adsorption or desorption occurred, and at equilibrium. Measurements were carried out both at constant temperatures and during temperature programmed desorption. The cross sections for helium scattering from deuterium and hydrogen on Fe(110) were found to be 3.4 \AA^2 and 3.5 \AA^2 , respectively. The cross section for D_2 scattering from adsorbed deuterium on Fe(110) was measured as 11.0 \AA^2 . The initial sticking coefficient and the rate of adsorption were found to be independent of temperature for both H_2 and D_2 . The desorption kinetics were found to be second order, with activation energies of 26.5 kcal/mole (D_2) and 25.0 kcal/mole (H_2). The isosteric heats of adsorption are 24.7 kcal/mole (D_2) and 24.2 kcal/mole (H_2).

INTRODUCTION

Because of its relevance to the problems of hydrocarbon catalysis on iron surfaces and the hydrogen embrittlement of ferrous alloys, the adsorption of hydrogen on iron surfaces has been studied by a number of investigators, utilizing a variety of experimental techniques. Among these are Bozso, et al. [1], who utilized thermal desorption spectroscopy (TDS), Auger spectroscopy, low energy electron diffraction (LEED), and work function measurements; Imbihl, et al. [2], and Moritz, et al. [3], who employed LEED; Baro and Erley [4] with high resolution electron loss spectroscopy; Kinzel, et al. [5], Muscat [6] and Pasco and Ficalora [7], who have performed theoretical analyses of this system.

Despite this effort, our understanding of the energetics and kinetics of the adsorption-desorption process is still incomplete. This is in part due to the inherent limitations of the experimental techniques used to date insofar as studies of hydrogen are concerned.

In the present work, two techniques not previously applied to this system are utilized, namely thermal energy atom scattering (TEAS) and angle resolved thermal desorption spectroscopy (ARTDS). Application of these techniques results in a more complete understanding of the adsorption of both hydrogen and deuterium on Fe(110). This paper presents the results of the TEAS measurements in detail, with emphasis on the strengths and pitfalls inherent in this recently developed technique. The companion paper presents the results of the ARTDS study and shows the detailed model of the adsorption-desorption process that can be obtained from the combination of both techniques.

Thermal energy atom scattering is a surface analytical technique wherein the intensity and/or shape of the specularly scattered beam arising from the scattering of gas atoms having energies in the range of 0.02 to 0.200 eV, is used to characterize surface structure, defect structure and adlayer coverage [8]. In the present context, the specular intensity can be directly related to adlayer coverage, and thus can be used to monitor surface concentration as the adsorption or desorption process occurs.

2. EXPERIMENTAL

2.1 Apparatus

All measurements were performed in an all metal ultrahigh vacuum system which has previously been described in detail [9]. This vacuum system included two differentially pumped chambers in which a helium beam was generated. The beam was modulated by a 50% duty cycle rotating chopper mounted in a buffer chamber. The source chamber was pumped by an untrapped diffusion pump. The base pressure in the source chamber was 3×10^{-8} torr. Both the buffer and main chamber were pumped by liquid nitrogen trapped diffusion pumps. Base pressures were 5×10^{-9} torr and 4×10^{-10} torr, respectively. The pressure in the main chamber rose to 1×10^{-9} torr when the beam was operating. The main chamber contained the sample, a cylindrical mirror electron energy analyzer, a monopole mass spectrometer and an ion gun.

The sample was an iron (110) single crystal, 1 cm in diameter and 0.05 cm thick, cut by electric discharge machining from an iron ribbon which had been recrystallized by the strain anneal technique. The sample could be heated from room temperature to 973 K in two minutes by direct

resistive heating and cooled from 973 K to 200 K in six minutes by flowing liquid nitrogen through supports near the sample. The sample temperature was measured by a W-5% Re, W-26% Re thermocouple spot welded near the edge of the backside of the sample.

The doubly-differentially-pumped detector chamber housed a quadrupole mass spectrometer. The axis of the detector chamber was fixed at 90° with respect to the molecular beam axis. Base pressure of the cryopumped detector chamber was 5×10^{-11} torr. The absolute molecular beam intensity was measured with a stagnation chamber mounted on the molecular beam axis. All molecular beams were incident on the sample at 45°.

2.2 Sample Cleaning

The major contaminants initially observed on the iron surface were carbon, sulfur and oxygen. This initial contamination was removed by cycles of argon ion bombardment at an energy of 1.8 KV and anneal at 973 K. During this thermal cycling, sulfur and carbon diffused from the bulk to the surface and were removed by further argon bombardment. It was not possible to produce an iron surface free of carbon by this method alone. In order to further clean the surface of the sample, it was necessary to expose it to oxygen at a pressure in the 10^{-7} torr range for a few minutes in order to create an iron surface partially covered by oxygen. The oxygen exposure was performed at temperatures below 373 K, as oxygen exposure above this temperature has been observed to cause faceting of the Fe(110) surface [10]. When the oxygen coverage reached the desired level, usually a half monolayer or less, oxygen exposure was discontinued and the sample was heated to the annealing temperature. The oxygen exposure-anneal cycle, which removed carbon by reaction to form CO, was repeated a number of times and the carbon contamination continued to

decrease. Sometimes oxygen remained on the surface after the cycle. In most cases, this oxygen could be removed by reannealing the sample. If this failed to remove the excess oxygen, it was removed by argon ion bombardment.

The combination of argon ion bombardment, oxygen exposure and anneal cycles reduced the contaminant level below the detectability limit of the Auger spectrometer. Carbon and oxygen were observed to build up on the surface of the iron sample overnight. These contaminants were easily removed by cycles of argon ion bombardment and anneal. It was rarely necessary to repeat oxygen exposure after the initial thorough cleaning of the sample.

Surface cleanness was monitored by both AES and helium scattering. After the Auger spectrum exhibited no further contaminants, continued cleaning resulted in further increases in the specularly scattered helium signal, indicating further improvements in surface cleanness. Cleaning was continued until the specular helium signal no longer increased with further cleaning. This maximum observed scattered helium intensity was reproducible and did not vary throughout these experiments.

Before each set of experiments, the cleanness of the sample was checked by both AES and helium scattering. Experiments were performed only when AES revealed no contamination and the specularly scattered helium signal reached the reproducible maximum intensity. An iron surface exhibiting these characteristics will be referred to as a clean surface throughout this paper.

2.3 Thermal Scattering

The effect of sample temperature on the intensity of the specular helium peak from a clean surface was monitored to provide the data

necessary to correct the intensity for temperature dependent surface vibrational effects unrelated to adsorption. The results of this investigation are shown in Figure 1. This clean surface response was reproducible when measured at different heating rates and upon rapid cooling. Thus, contamination effects are negligible.

Attempts were made to analyze this data with respect to three of the current theories concerning Debye-Waller corrections to molecular beam scattering. These corrections are described in detail by Beeby [11], Weinberg [12], and Lapujoulade, et al [13]. However, in all cases the data could not be well modeled by these theories. The reason for this discrepancy is not clear. Goodman [14] has questioned the general validity of the application of a Debye-Waller type relationship to atomic scattering.

2.4 Adsorption Studies

Measurements of helium specular scattering were performed while adsorption and desorption were taking place at constant surface temperature. In these experiments, the specular helium beam intensity was monitored while the sample was exposed to static pressures of H_2 or D_2 at surface temperatures ranging from 200 K to 500 K. Starting with a clean surface, hydrogen or deuterium was rapidly introduced into the system and brought to a constant pressure. As the hydrogen or deuterium adsorbed onto the sample surface, the intensity of the scattered helium signal decreased, enabling the adsorption process to be observed.

The intensity of the scattered helium beam was also monitored at a constant H_2 or D_2 pressure after equilibrium had been established. The gas was then rapidly removed from the system. As the hydrogen or deuterium desorbed from the surface, the increase of the specular helium

signal was monitored.

Helium scattering was also used to monitor temperature programmed desorption. In these experiments, as in normal TDS experiments, the sample was first cleaned, annealed and cooled to the desired temperature (200 K). The surface was then examined by both AES and helium scattering to insure surface cleanness. The sample was exposed to hydrogen or deuterium for a given time and partial pressure and then heated linearly with time at 15 K/sec through the range where desorption occurred. The major difference between this process and conventional TDS experiments is that, in the helium-monitored process, the surface coverage is probed directly, rather than being inferred from the desorption rate, which is the parameter monitored by conventional TDS. As the temperature of the sample increased, the hydrogen or deuterium desorbed and the specularly scattered helium intensity increased. As the coverage approached zero, the intensity of the specularly scattered beam approached that obtained from a clean surface at that temperature. Helium scattering TDS experiments, which are directly surface sensitive, are insensitive to the velocity distribution of the desorbing particles, a factor which may complicate the analysis of standard TDS data.

3. RESULTS AND ANALYSIS

3.1 Relation of Scattered Intensity to Coverage

In order to use the height of the specular peak as a measure of adsorbate coverage, it was first necessary to show that the shape of this peak does not vary with adsorbate coverage. If this is true, the peak height alone can be used to monitor surface coverage, rather than the peak area. The independence of peak shape on adsorbate coverage was verified

as shown in Figure 2. In this figure, solid dots represent the scattered helium intensity as a function of angle for scattering from a clean surface at 311 K. The circles represent scattering from a surface at 311 K after an exposure of 6.5 L of deuterium (sufficient to develop a coverage of 0.4 monolayers). The adsorbate coverage reduces the absolute scattered intensity. Multiplying each of these points by a constant factor of 1.28, as shown by the X's in the figure, shows that while the intensity has decreased, the peak shape has not changed. Similar results were obtained with adsorbed hydrogen.

The width of the specularly scattered beam arises from two factors; instrumental effects and surface imperfection. The instrumental broadening of the specular beam has two sources: the beam has a finite angular divergence and the detector has a finite aperture. The measured specular beam width in our apparatus is equal to the calculated instrumental broadening determined from these two effects. Lapujoulade [15,16] has shown that defect densities as high as one every ten surface sites broaden the full width at half maximum by only 0.6° , while defect densities of one every 33 sites and one in 100 produce broadenings of only 0.2° and 0.1° , respectively. Measurements of the peak shape to this accuracy were not possible. Thus broadening due to surface defects could not be observed.

Since the peak shape is independent of coverage, the scattered intensity, I , is a function of adsorbate coverage, θ ; $I = f_1(\theta)$. This formulation does not yield a unique relation between peak height and coverage, since the peak height is also strongly affected by temperature dependent surface vibrational effects, as was shown in Figure 1. These effects can be accounted for by defining

$$(I/I_0)_T = f(\theta) , \quad (1)$$

where I and I_0 are peak heights measured at the same temperature, T , on the covered and clean surfaces respectively.

As we will see later, the scattering cross section for helium from hydrogen and deuterium on Fe(110), $\Sigma^{\text{He}}_{\text{ads}}$, is smaller than the adsorption site size, σ . The relationship between scattered intensity and coverage for this case is [17]

$$(I/I_0) = 1 - \alpha \theta, \quad (2)$$

where $\alpha = \Sigma^{\text{He}}_{\text{ads}}/\sigma$.

3.2 Isothermal Adsorption-Desorption Studies

Isothermal experiments were performed wherein the intensity of the scattered helium beam was monitored versus time over a range of constant deuterium pressures. Typical results are shown in Figures 3A and 3B. These curves exhibit the temporal response of the specularly scattered helium intensity when the deuterium pressure was rapidly increased or decreased. An arrow indicates the time at which the deuterium pressure was stabilized. When attempting to attain large deuterium pressure changes, spikes were often seen in the detected intensity. It is believed that when the deuterium pressure was rapidly increased or decreased, a mass spectrometer signal was created which was temporarily in-phase with the scattered helium signal. (D_2 and He have essentially the same mass.) These spikes were never observed when the identical experiments were performed with hydrogen rather than deuterium,

or if the valve was opened or closed slowly.

As shown by Poelsema et al [18], the scattering cross section for diffuse helium scattering from an adsorbate can be calculated from the initial slope of this data through the following equation:

$$[d(I/I_0)/dt]_{t=0} = P_{ads}/(2\pi mkT)^{\frac{1}{2}} \cdot 2S_0 \Sigma_{ads}^{He} , \quad (3)$$

where $(d(I/I_0)/dt)_{t=0}$ is the initial slope of the data at a given temperature, $P_{ads}/(2\pi mkT)^{\frac{1}{2}}$ is the adsorbate impingement rate and S_0 is the initial sticking coefficient at the same temperature. Using the initial slope at this curve at 200 K and S_0 at 200 K (obtained from TDS experiments discussed in Part II) yields a scattering cross section for diffuse helium scattering from deuterium on Fe(110) of $3.36 \pm 0.17 \text{ \AA}^2$ which is smaller than the site size of 5.81 \AA^2 . Thus α is 0.58.

Ascertaining Σ_D^{He} enabled the determination of S_0 as a function of temperature. The results of this calculation are shown in Figure 4. The initial sticking coefficients are nearly identical below 323 K. There appears to be a slight increase above this temperature but the change is well within the experimental error.

Analysis of the temporal response of the coverage while deuterium was present yielded information on the kinetics of deuterium adsorption on Fe(110). The isothermal adsorption rate as a function of deuterium pressure was independent of surface temperature. The rate of adsorption was well described by the relation

$$R_a = 2S(\theta)J/N , \quad (4)$$

where J is the molecular impingement rate, N is the number of adsorption sites per unit area and $S(\theta)$ is the sticking coefficient as a function of coverage, θ . The observed dependence of adlayer coverage on deuterium exposure, for a sample temperature of 200 K is shown in Figure 5. The sticking coefficient as a function of coverage, which was derived from the slope of this curve, is shown in Figure 6. Over most of the coverage range studied, this curve exhibits the linear relation between $S(\theta)$ and $(1-\theta)^2$ expected for direct dissociative adsorption. This point is discussed in greater detail in Part II of this work.

Analysis of the desorption process occurring when the deuterium was turned off confirmed second order desorption of deuterium from Fe(110), as has been observed by TDS (see Part II). Figure 7 exhibits the expected linear behavior for second order desorption. A plot of the log of the rate constant versus temperature yielded a straight line, from which an activation energy for desorption of 26.1 ± 1.0 kcal/mole and a pre-exponential of $(8.1 \pm 2.3) \times 10^{-3}$ cm²/molecule sec were calculated.

Equilibrium adsorption isotherms were constructed from the isothermal data at steady state. The equilibrium isotherms are defined as the relative steady state scattered peak height decrease as a function of deuterium pressure at a constant surface temperature. Isosteres were deduced from these isotherms and are shown in Figure 8. The slope of an isostere is equal to $\Delta H_{\text{ads}}/R$, where H_{ads} is the heat of adsorption. The isosteres are very nearly parallel. The average heat of adsorption for deuterium on Fe(110), calculated from the isosteres, is 24.7 ± 2.9 kcal/mole.

3.3 Temperature Programmed Desorption

As previously discussed, modified TDS experiments were performed wherein the adlayer coverage was monitored by the helium beam as the temperature was increased. Typical results are shown in Figure 9. These raw data were corrected for surface vibrational effects, using the data in Figure 1, and converted to coverage versus temperature using Equation 2. Results of this calculation are shown in Figure 10. Equations relating the adsorbate coverage to temperature have been derived by a number of authors [19]. For a second order desorption process with the activation energy for desorption, E_d , and pre-exponential, ν , both assumed to be independent of coverage, the appropriate equation is

$$1/\theta - 1/\theta_i = (N\nu R/\beta E_d)[T^2 \exp(-E_d/RT) - T_i^2 \exp(-E_d/RT_i)] \quad (5)$$

where T is the instantaneous temperature, T_i is the initial temperature, N is the number of surface sites/cm², β is the heating rate, θ_i is the initial coverage and θ is the coverage at T . Fitting this equation to the data, as shown by the solid lines on Figure 10, yielded values of $E_d = 26.4 \pm 1.2$ kcal/mole and $\nu = (5.1 \pm 1.7) \times 10^{-3}$ cm²/molecule sec for $\theta < 0.6$. The results obtained from the helium scattering TDS experiments are in excellent agreement with those obtained from isothermal desorption and conventional TDS. A direct comparison with conventional TDS is given in Part II of this work.

3.4 Studies with Hydrogen

Identical experiments were performed with hydrogen. The cross section for helium scattering from hydrogen adsorbed on Fe(110) was found

to be $3.47 \pm 0.35 \text{ \AA}^2$. He TDS experiments yielded values of $E_d = 25.2 \pm 1.5 \text{ kcal/mole}$ and $\nu = (1.9 \pm 0.4) \times 10^{-3} \text{ cm}^2/\text{molecule sec}$.

As was the case for deuterium, the initial sticking coefficient and the rate of adsorption as a function of coverage were both independent of sample temperature. The plot of $1/\theta$ versus time for isothermal hydrogen desorption was found to be linear, indicating second order kinetics. An activation energy for desorption of $25.1 \pm 1.3 \text{ kcal/mole}$ and a second order pre-exponential of $(3.5 \pm 1.5) \times 10^{-3} \text{ cm}^2/\text{molecule sec}$ were calculated from this experimental data. The average heat of adsorption for hydrogen on Fe(110), as obtained from equilibrium isosteres, was $24.2 \pm 2.4 \text{ kcal/mole}$.

3.5 Deuterium Scattering

An additional set of experiments was performed which will be described briefly. These experiments were performed in a different vacuum system, which has been described in detail elsewhere [9]. In these experiments, a molecular deuterium beam was used to study deuterium adsorption on Fe(110). The deuterium beam was used as a simultaneous probe and dosing source. Typical results for the scattered intensity versus time are shown in Figure 11. The equivalent deuterium pressure at the surface was $1.25 \times 10^{-7} \text{ torr}$ in all cases. The cross section for deuterium scattering from deuterium on Fe(110) was found to be $11.0 \pm 1.9 \text{ \AA}^2$. This is 3.3 times greater than the cross section for helium scattering from deuterium on Fe(110). Coverage vs. exposure data derived from the curves of Figure 11 were in good agreement with those derived from helium scattering data. The extent of this agreement is shown in Figure 12, which compares measurements made at 400K using the two

techniques.

4. DISCUSSION

Helium atomic and deuterium molecular beam scattering have been shown to be sensitive, useful techniques in the investigation of hydrogen and deuterium adsorption on Fe(110). The technique does not perturb the surface and is insensitive to artifacts associated with the directionality of desorption. The small scattering cross sections are somewhat surprising but in reasonable agreement with the work of Poelsema [20] for hydrogen on platinum (S)-9(111) X (111), who found a value of $\Sigma^{\text{He}}_{\text{H}} = 8.65 \text{ \AA}^2$ for this surface, using the specularly scattered peak from a helium beam incident at an angle of 85° . The difference between this value and those found in the present study may indicate that the hydrogen atom is held closer to the surface on the relatively open Fe(110) surface.

The results reported in this paper are quite different from those reported in our earlier paper [21], which we now believe to be spurious. It is believed that in the earlier experiments the high deuterium beam intensity increased the rate of sputtering at an ion pump surface. Large cross section contaminants were released from the pump and subsequently adsorbed on the sample surface. Due to the high sensitivity of the deuterium specular scattering technique, these contaminants caused significant scattering of the deuterium beam at concentrations too low to be observed by AES. Under these conditions, the decrease in the specular intensity of the deuterium beam was primarily due to the presence of these contaminants, rather than the adsorbed deuterium. The kinetics derived from isothermal deuterium scattering were thus the kinetics of contaminant adsorption rather than deuterium adsorption. This reveals an important

consideration in the performance of molecular beam scattering experiments. The technique is extremely sensitive to the presence of adsorbed particles. It does not, however, discriminate between various adsorbates. All adsorbates lead to a change in the specularly scattered intensity. The experimentalist must be extremely careful to eliminate possible sources of contamination. This is especially important when the contaminant materials may have a high scattering cross section compared to that of the material under study.

Specific conclusions concerning the adsorption kinetics of H_2/D_2 on Fe(110), and a comparison of results obtained by TEAS and ARTDS techniques, are presented in Part II of this work.

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FIGURE CAPTIONS

Figure 1: Temperature dependence of the specular helium scattering intensity from clean Fe(110).

Figure 2: Effect of deuterium adsorption on specular helium scattering from Fe(110) at 311 K: (•) clean surface, (o) after exposure to 6.5 L of D₂, (x) points from adsorbate-covered surface, multiplied by 1.28.

Figure 3: Helium specular intensity as a function of time during exposure of Fe(110) surface to deuterium at 407 K:

a: $P_{D_2} = 1.3 \times 10^{-7}$ torr;

b: $P_{D_2} = 2.1 \times 10^{-6}$ torr.

Arrows indicate time at which deuterium pressure stabilized. Spikes in curve b are artifacts arising from interference of D₂ molecules with the He mass spectrometer signal.

Figure 4: Initial sticking coefficient, S_0 , for deuterium adsorption on Fe(110) as a function of surface temperature.

Figure 5: Deuterium adlayer coverage as a function of exposure at 200 K on the Fe(110) surface, as deduced from adsorption transients.

Figure 6: Sticking coefficient for deuterium adsorption on Fe(110) as a function of adlayer coverage, deduced from adsorption transients.

Figure 7: Kinetic plot of deuterium desorption rate from Fe(110).

T = 407 K. Linear behavior of $1/\theta$ vs t indicates second order kinetics.

- Figure 8: Equilibrium isosteres for the adsorption of deuterium on Fe(110), derived from equilibrium coverage data determined from helium specular intensity attenuation, I/I_0 .
- Figure 9: Thermal desorption traces for the desorption of deuterium from Fe(110), as monitored by helium specular intensity attenuation.
- Figure 10: Deuterium adlayer coverage as a function of temperature during thermal desorption. Results deduced from helium scattering studies. Solid lines are fits to Equation 5.
- Figure 11: Specular intensity attenuation as a function of time for a D_2 molecular beam scattered from an Fe(110) surface. The attenuation is due to deuterium adsorption from the beam.
- Figure 12: Comparison of deuterium adlayer coverage as a function of exposure deduced from helium scattering (---) and deuterium scattering (—) measurements.

FIGURE 1- EA KUB8 FJ.M. M.D. 10-1-1

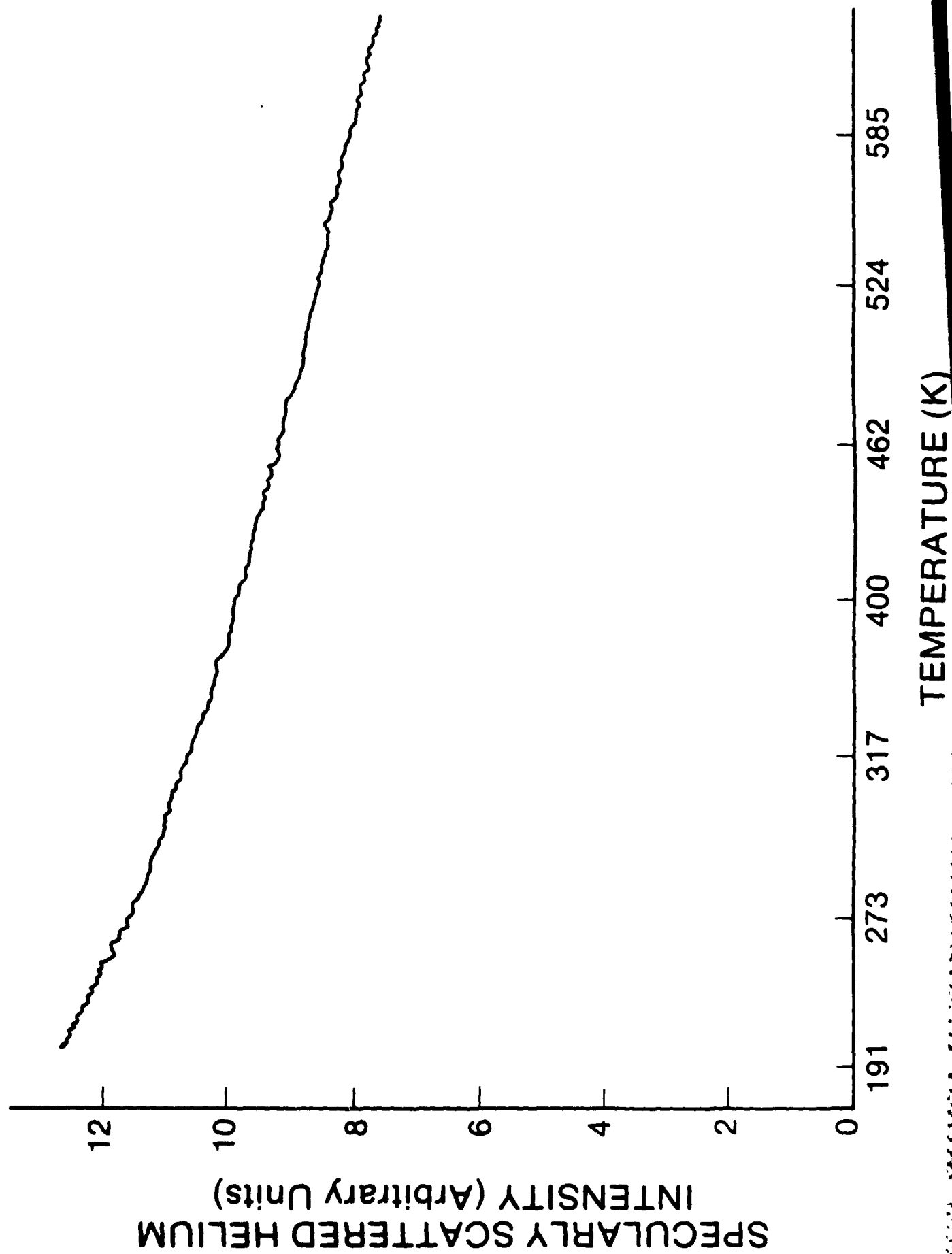


FIGURE 2 : C. A. R. 123 J. B. H. 123 1 3

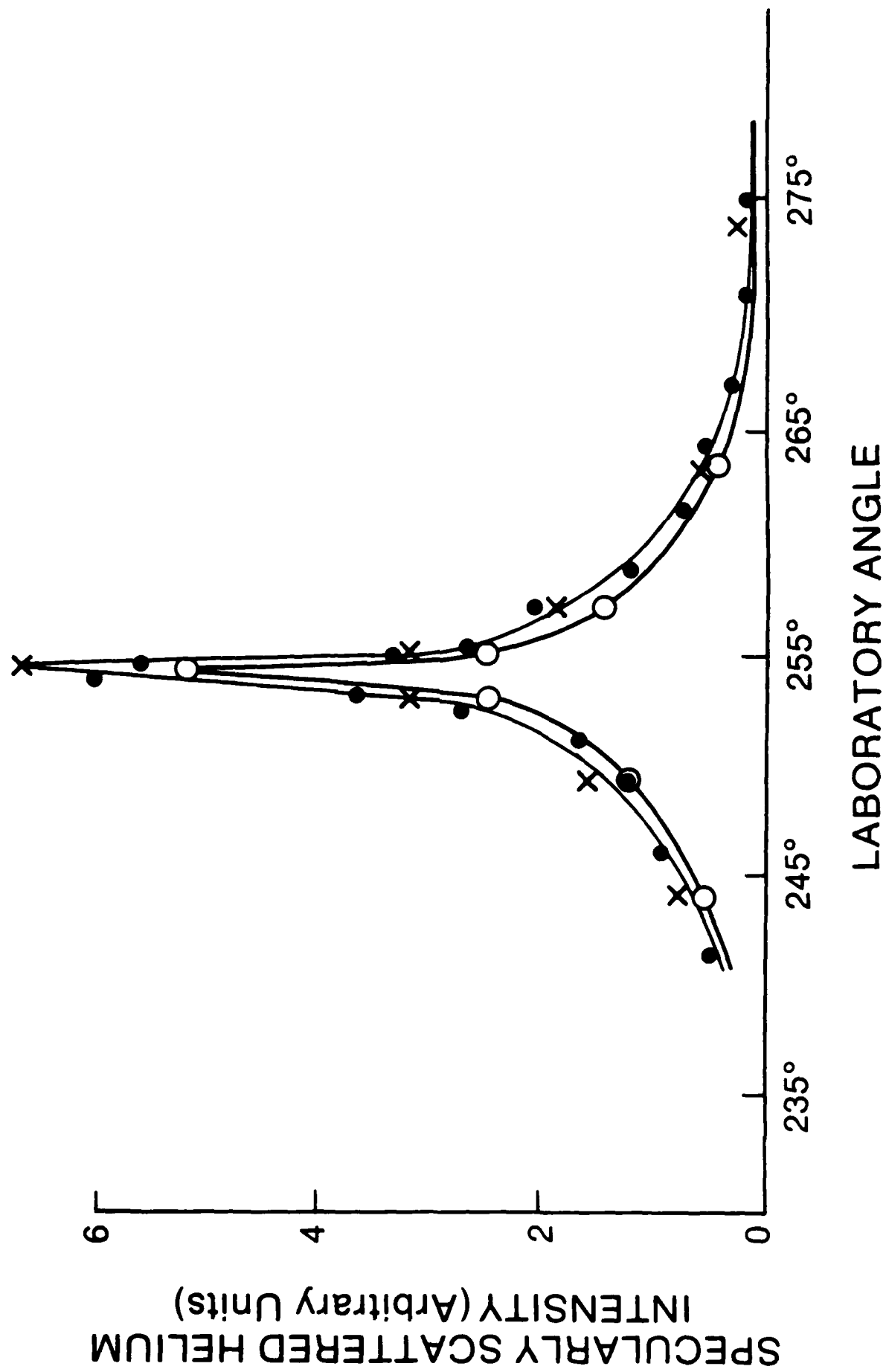


FIGURE 3a: EARLE & J. H. HADSON - I

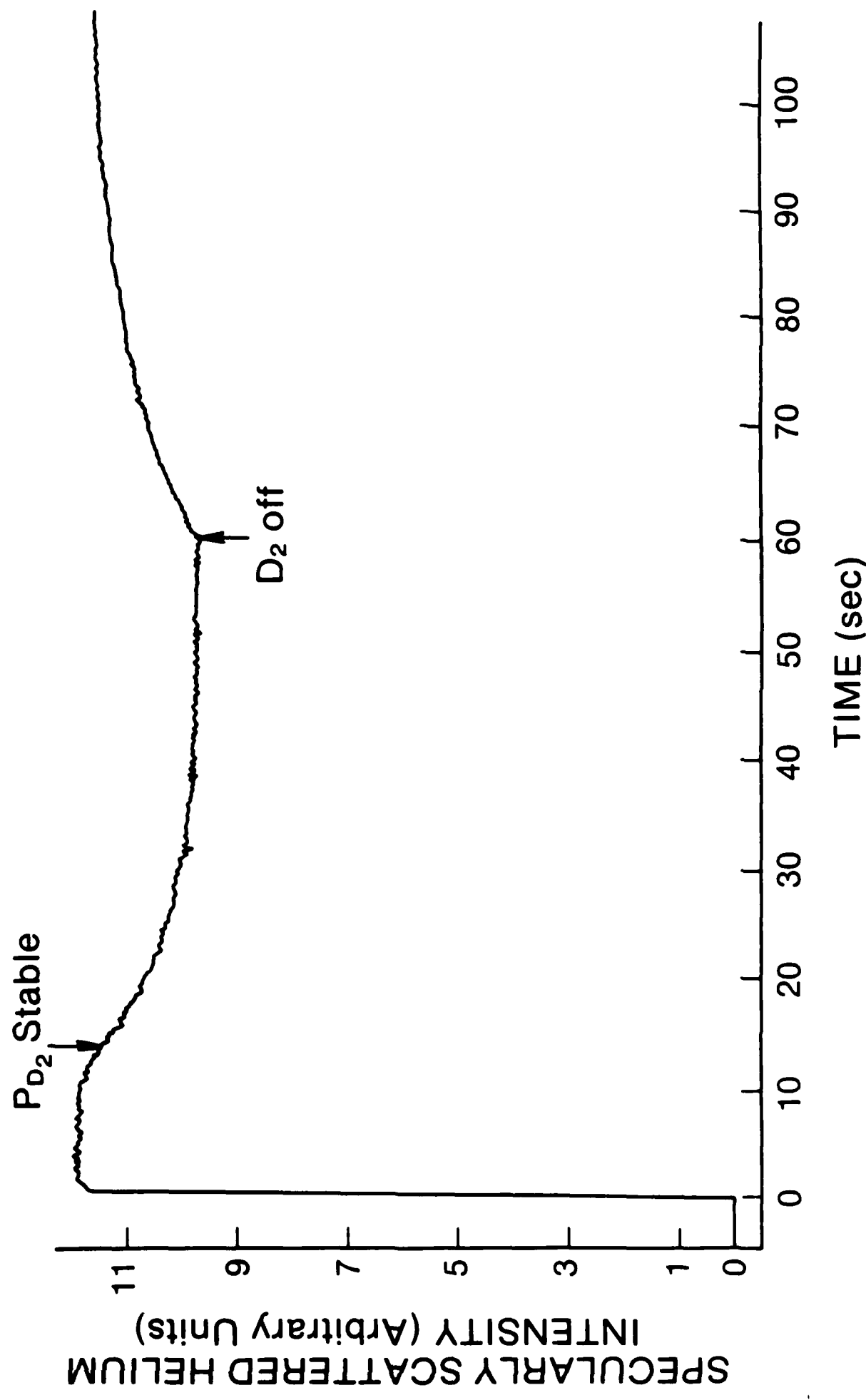


FIGURE 36: E.A. KUZNETS & J.B. HUDSON - I

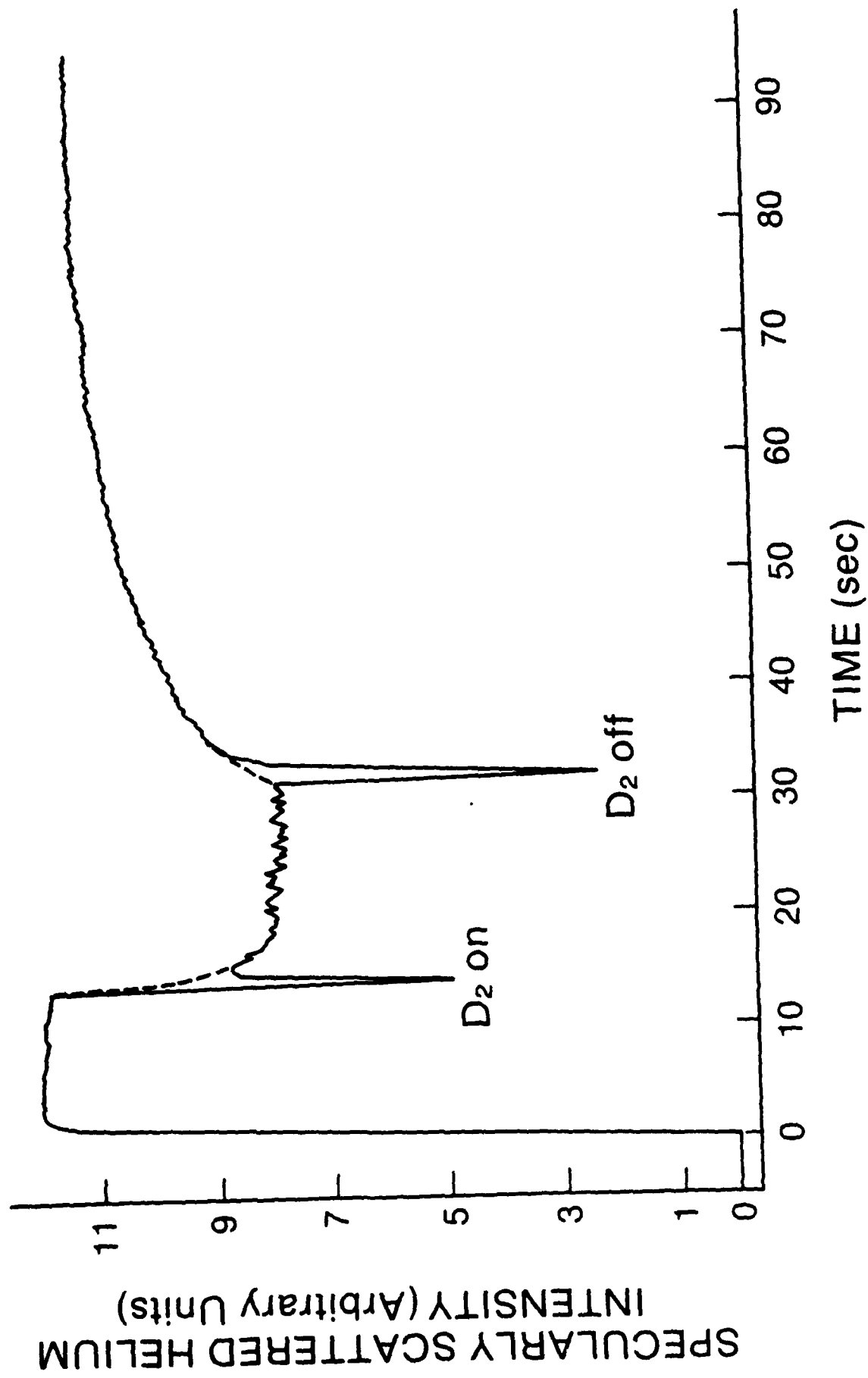


FIGURE 4. E.A. RUDOLPH, J.R. MURPHY, I.

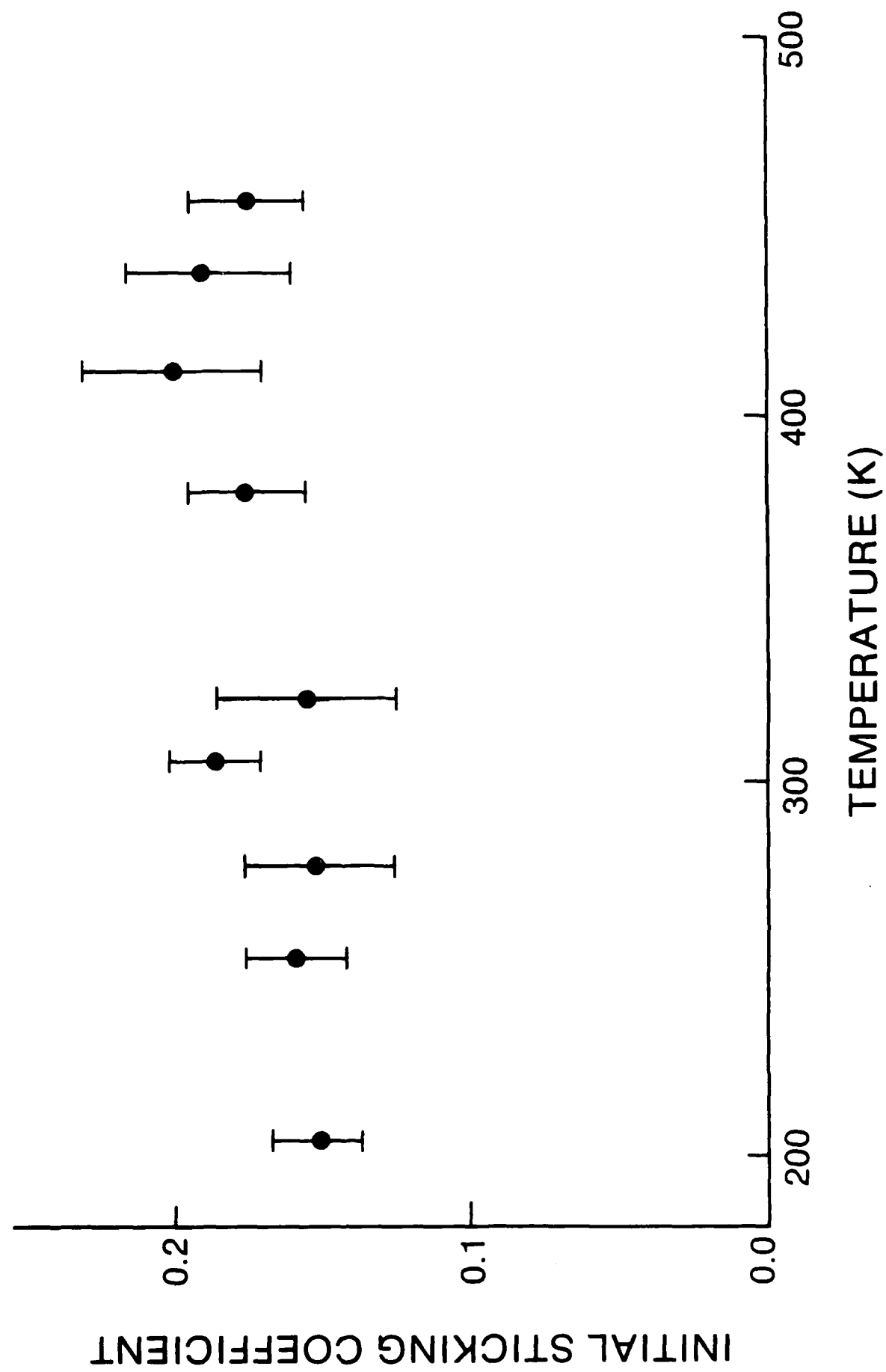


FIGURE 5: E.A. KULEZ $\dot{\text{P}}$ J.B. HUDSON - I

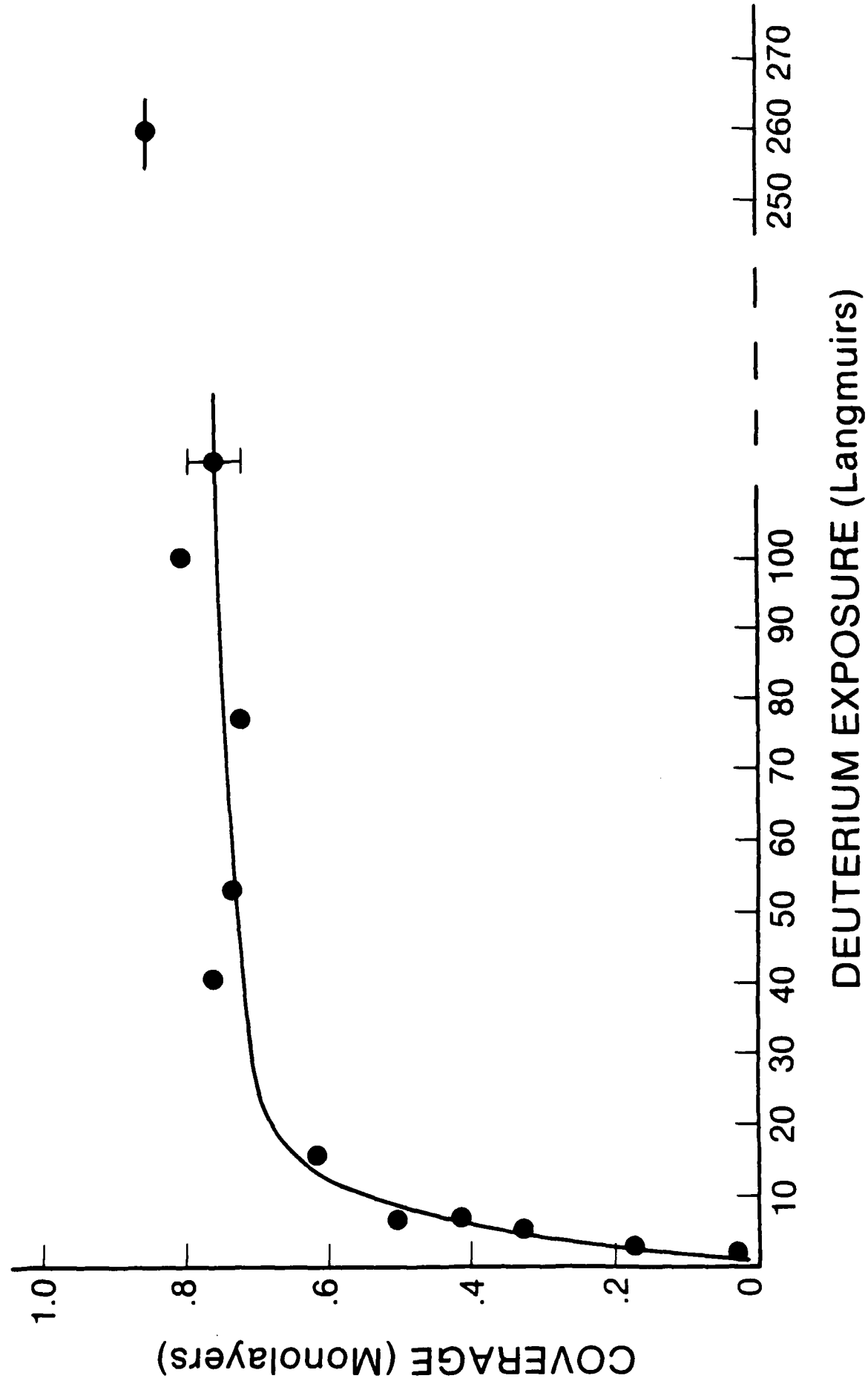


FIGURE 6. $\epsilon^2 H$ vs $\epsilon^2 H$ for $H = 1.0$

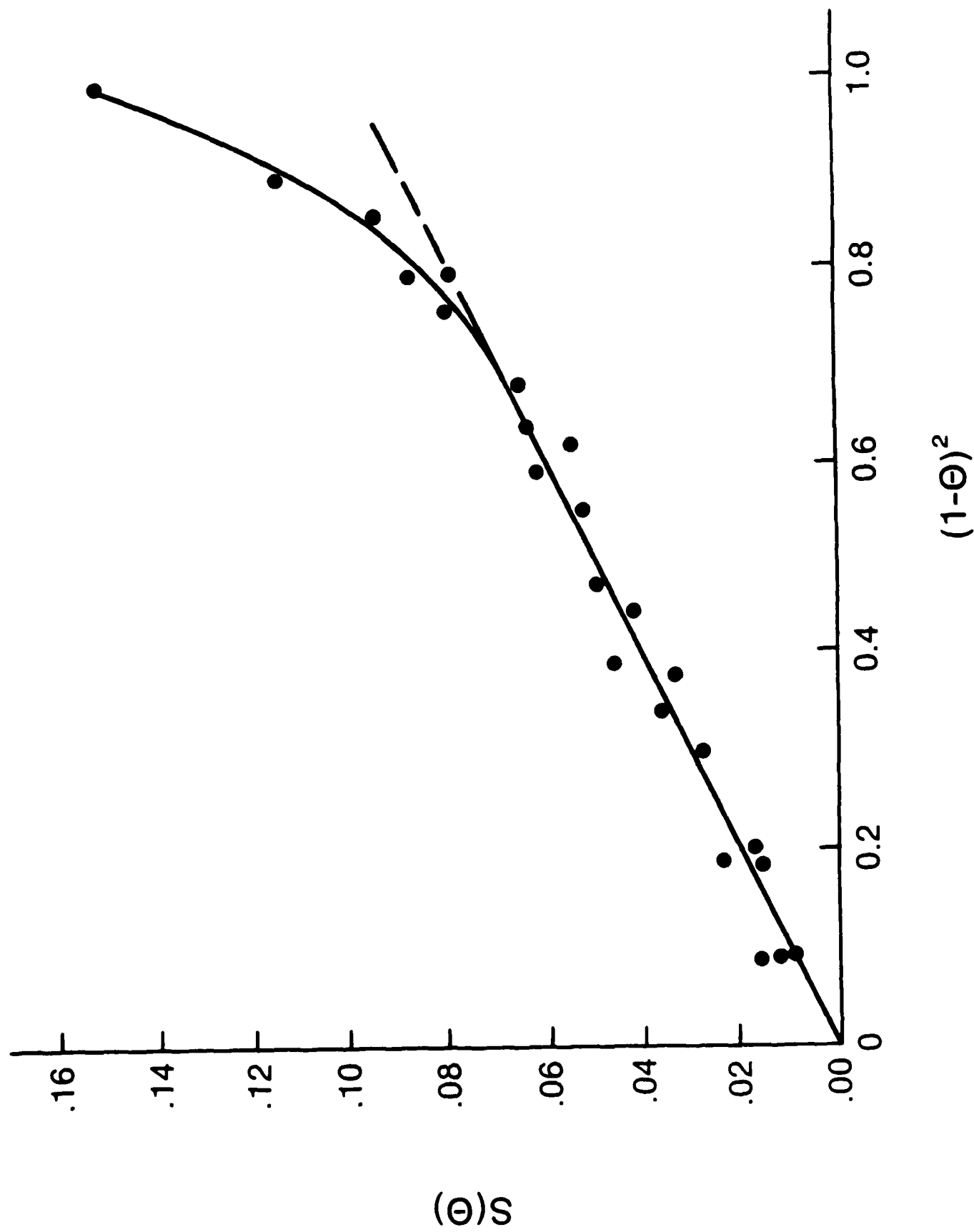


FIGURE 7: E.A. AND J. L. 1000 1-1

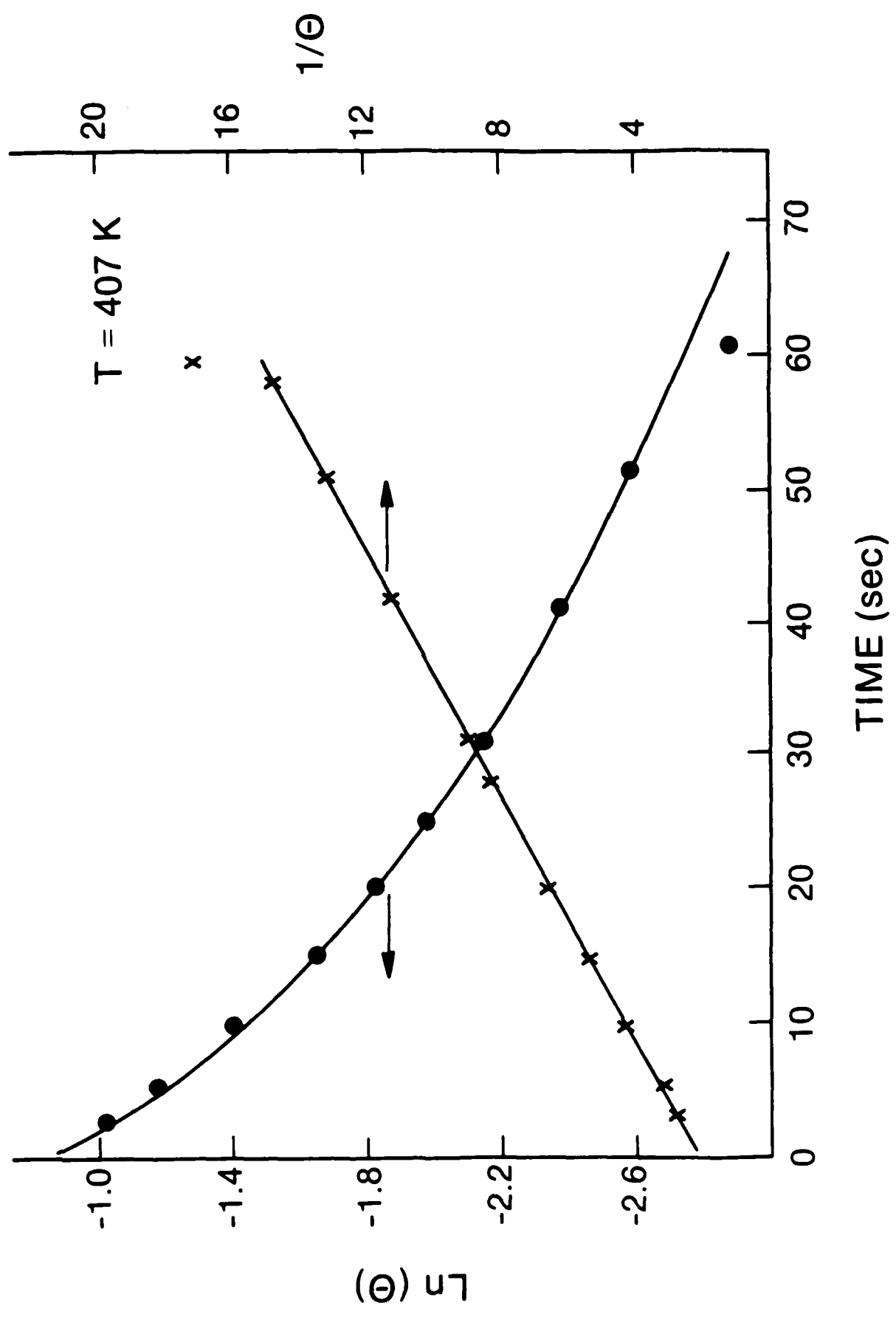


FIGURE 8. E. A. KULEZ' & J. R. HULSON-V

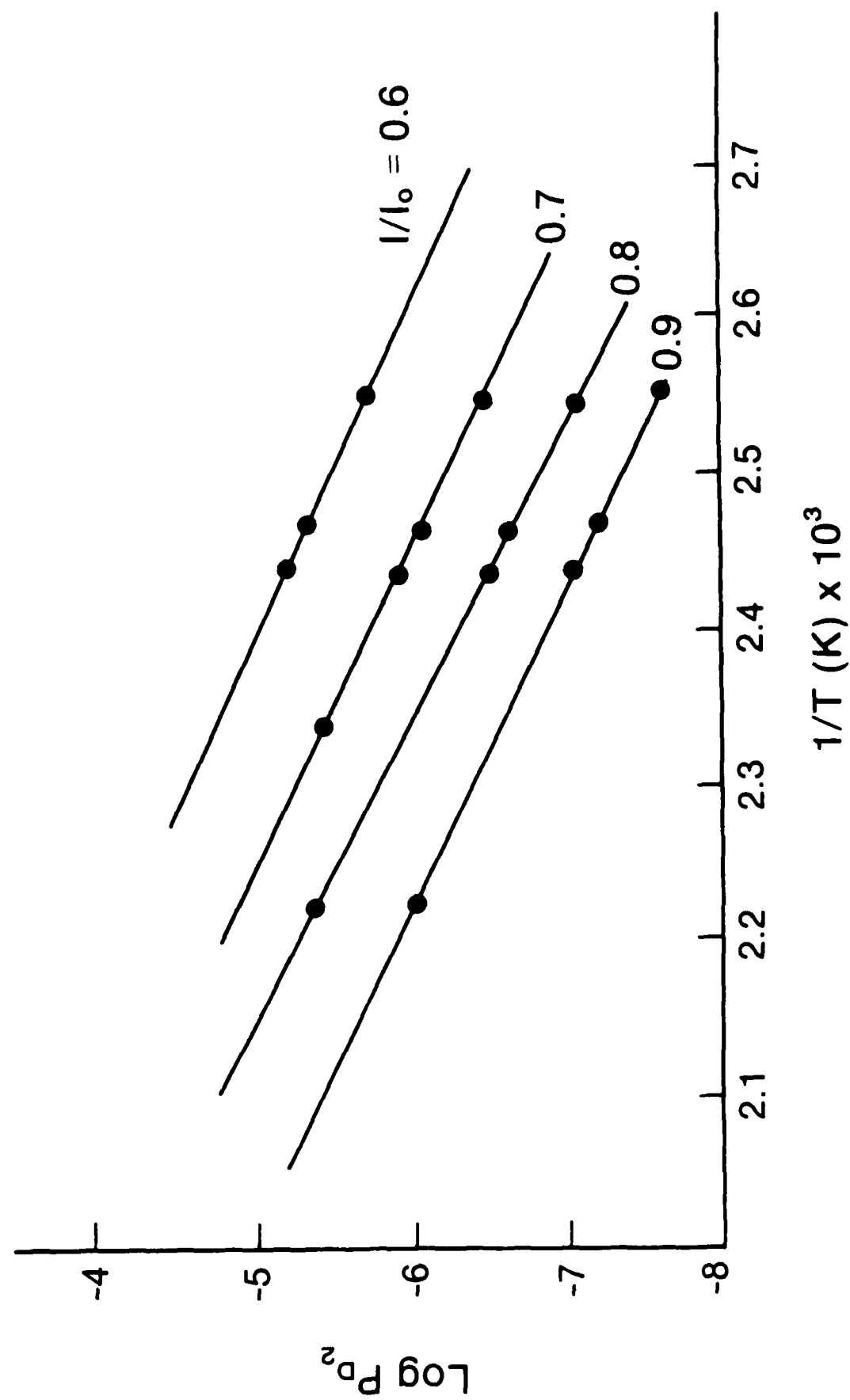


FIGURE 9. E. A. KILB & J. A. MASON, 1967

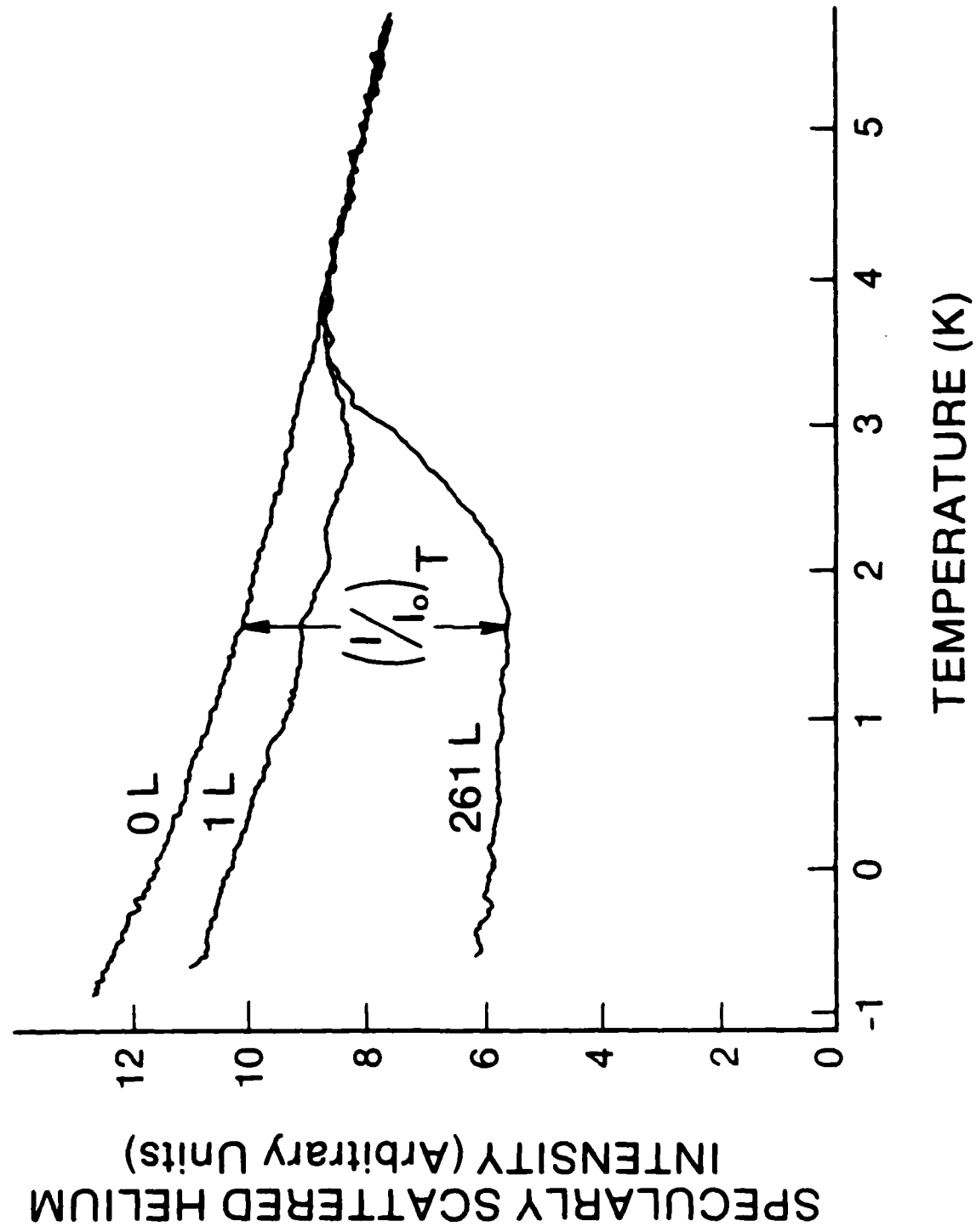
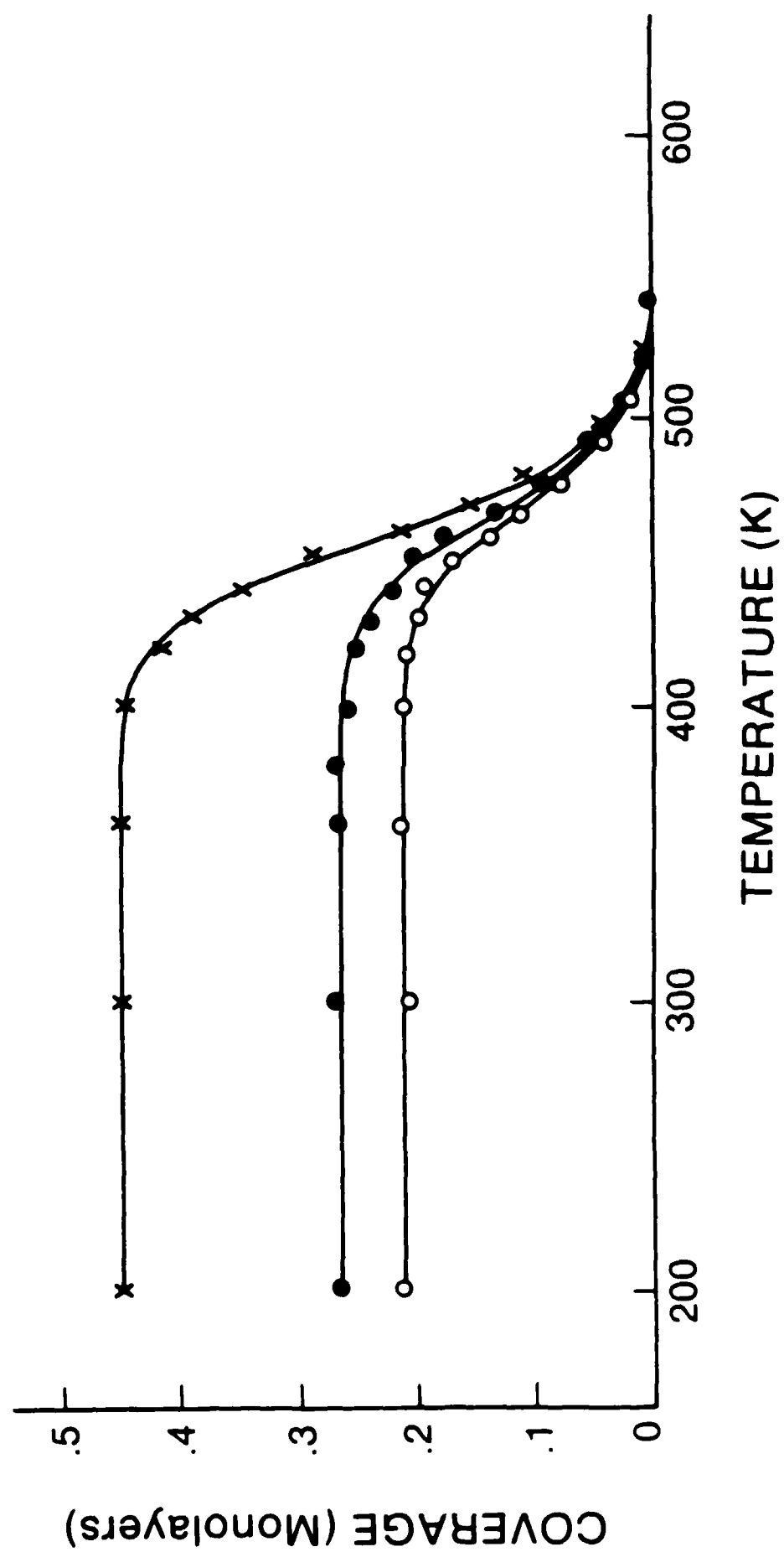
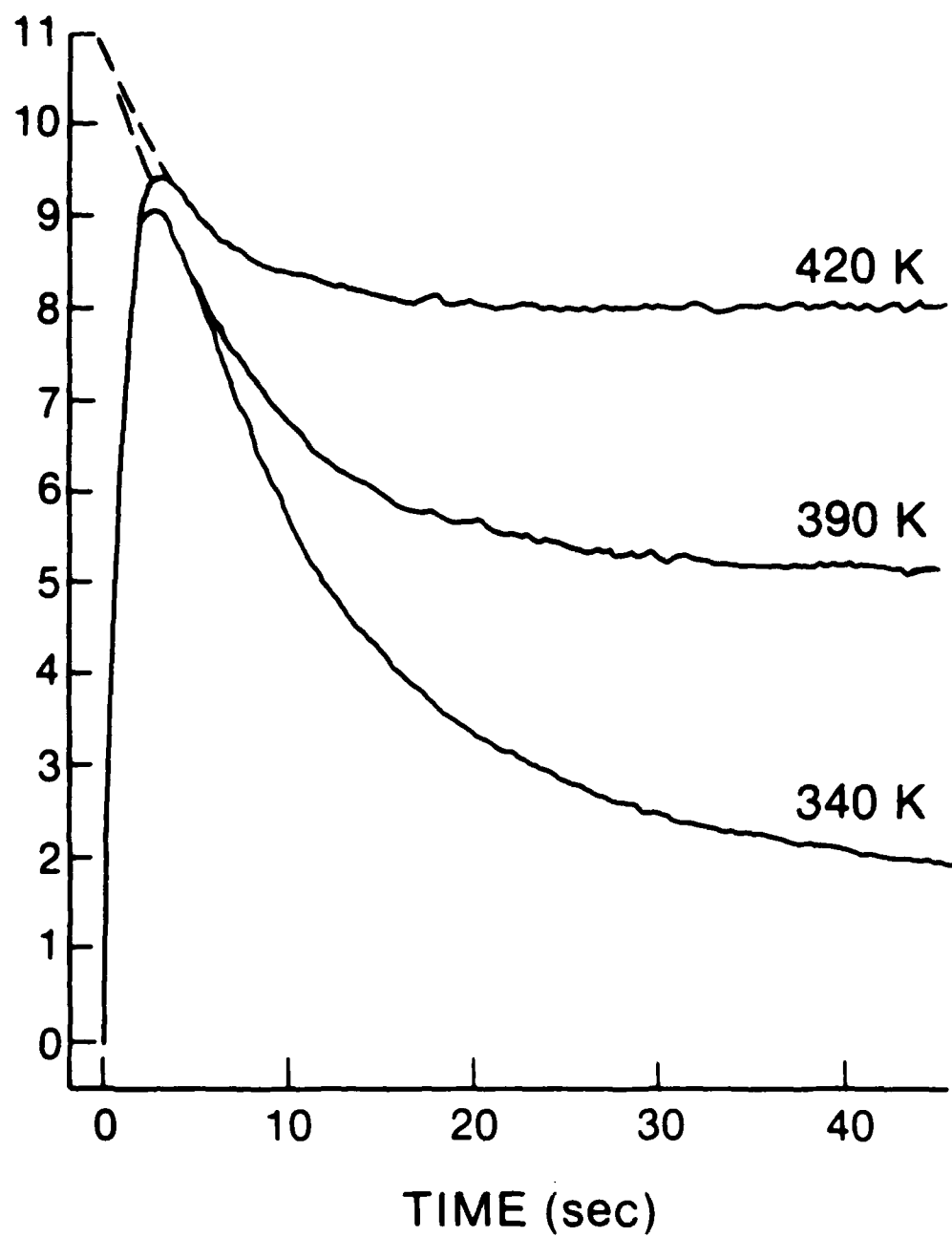
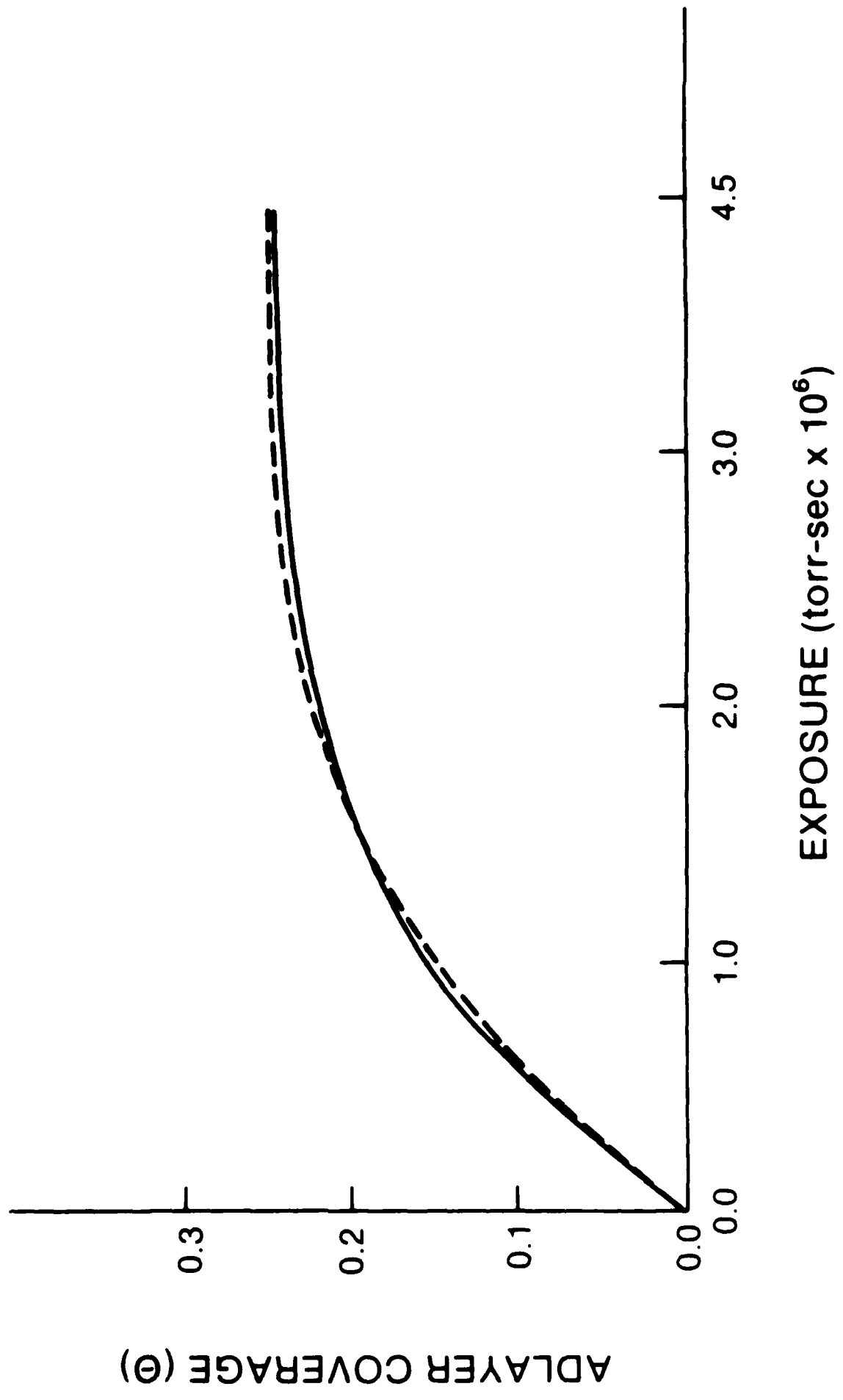


FIGURE 10: E.A. KULEZ' & J.P. HUDSON - I



**SPECULARLY SCATTERED HELIUM
INTENSITY (Arbitrary Units)**





END

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